The role of acid sites in cobalt zeolite catalysts for selective catalytic reduction of NO_x

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The role of the acidic support in ion-exchanged cobalt-zeolite, lean NO_x catalysts has been determined by studying the individual steps in the selective reduction pathway. At a GHSV of 10,000 and reaction temperatures below 400 °C, NO oxidation is not sufficiently rapid to obtain equilibrium over, for example, 1–4 wt% Co-mordenite catalysts. The NO oxidation rate increases in the order $H^+ < Co^{2+} <$ Co oxide, and neither the number, nor the strength of the acid sites affects the specific rate of the Co^{2+} ions. For reduction of NO_2 by propylene at 300 °C and methane at 400 °C, the formation of N_2 is suggested to occur at support protons sites. In addition, the rate of N_2 formation increases linearly with an increase in the number of acid sites, and the specific activity increases with an increase in acid strength. Cobalt (2+) ions do not contribute significantly to the formation of N_2, but do non-selectively reduce NO_2 to NO. It is proposed that the formation of N_2 occurs by protonation of the reducing agent followed by attack of the carbocation by gas phase NO_2. Thus, the selective reduction of NO requires two catalytic functions, metal and acid sites.

Keywords: selective catalytic reduction, lean NO_x, Co-ZSM-5, Co-mordenite, NO_2 reduction, NO oxidation

1. Introduction

Over the last several years, much research has been directed at the development of new catalysts, which in the presence of excess O_2, will reduce NO_x by hydrocarbons in engine exhaust [1–4]. Such a catalyst would permit better exhaust clean-up of diesel engines, and permit greater fuel efficiency of gasoline and natural gas engines while meeting federally mandated emission standards.

One family of catalysts which has been extensively investigated for these applications is metal-exchanged zeolites [3], for example, Cu [5–9], Ga [4,10–12], Ce [13–15] and, especially, Co [1,16–24]. While it is recognized that the most active catalysts are associated with the strongly acidic zeolites [4,10,15–17], such as ZSM-5 and mordenite, the role of zeolite remains unclear [3,4,10,12,25]. It has been postulated that certain zeolite topologies result in metal ion coordination geometries which are more catalytically effective for NO_x reduction [10,25], or that the zeolite crystal field may promote the reaction [10]. Alternatively, protons have been proposed as catalytic sites for NO oxidation [12] and hydrocarbon activation [2].

There has evolved general agreement that the first step in the selective catalytic reduction of NO_x is oxidation of NO to NO_2 and that this reaction is catalyzed by metal oxides and ions [12,13,18–24]. There is, however, disagreement about the rate of this reaction. Since the rate of N_2 formation from $NO + O_2$ was identical to that with NO_2, it was concluded that NO oxidation is rapid and in equilibrium [19,25]. Independent measurement of the rate confirms that over active catalysts [24], at low space velocities [26], and high reaction temperatures [27] NO oxidation is in equilibrium. For many catalysts, however, at reaction temperatures below about 400 °C, NO oxidation is slow and does not attain equilibrium [24,27,28].

Following NO oxidation, by a complex series of reactions NO_2 is converted to N_2. Although this reaction is often assumed to be rate limiting [19,20,22,29], catalyst evaluations and mechanistic studies often use gas compositions of $NO + O_2 +$ hydrocarbon. However, because the rate of NO oxidation may be slow, the formation of N_2 may not be rate determining. Under such conditions, any change in the catalyst composition which leads to an increase in the overall rate of N_2 formation may be due to either an increase in the rate of NO oxidation, resulting from an increase in the NO_2 concentration, or due to an increase in the rate of NO_2 reduction. In order to determine which reaction has been affected by the catalyst change, it is necessary to study the individual reactions separately.

In order to better evaluate the role of the acidic support on the performance of cobalt-exchanged, lean NO_x catalysts, the two reactions, NO oxidation and NO_2 reduction, have been studied separately using both propylene and methane as reducing agents. Catalysts with and without Co were compared and included zeolites known for their high activity, like mordenite and ZSM-5, and those which are poorly active, like Y-zeolite and silica–alumina. In addition, for mordenite both the amount of ion-exchanged cobalt and protons were varied.

With the current letter, we wish to report that the number and strength of acid sites does not influence the NO oxidation rate of Co^{2+} ions. However, the formation of N_2

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occurs at the proton sites, and the activity per H^+ increases with increasing acid strength. Furthermore, Co^{2+} ions do not significantly contribute to the formation of N_2.

2. Experimental

2.1. Catalysts

H-ZSM-5 (CBV-5020, 1.8 wt% Al), H-mordenite (CBV-30A, 2.6 wt% Al) and Na-mordenite (CBV-10A, 5.6 wt% Al) were commercial zeolites obtained from Conteka B.V. (now PQ Silica). H-USY (LZY-84) and silica–alumina (grade 135) were obtained from UOP and Aldrich, respectively.

The cobalt catalysts were prepared by conventional ion exchange with cobalt nitrate. In order to obtain 1 wt% Co, the zeolite was exchanged with a limited amount of cobalt nitrate. For example, 1.5 g $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 200 ml H_2O was added to 25 g of H-mordenite (H-MOR) (about 1.2 wt% Co based on the amount of support). The zeolite was heated to 60 °C for 3 h and filtered. The Co/H-MOR was re-slurried in 200 ml of hot H_2O for 2 h, filtered, dried overnight at 100 °C and calcined by heating at 1 °C/min in flowing air to 450 °C and holding for 1 h. The color of the Co^{2+}-exchanged zeolites was pink, while the $Co/SiO_2–Al_2O_3$ was blue. Co exchange of Na-MOR also resulted in the partial exchange of Na^+ by H^+ ions. 100 g of Na-MOR was ammonium-exchanged with 3 × 500 ml of 2 M NH_4NO_3 and calcined at 450 °C prior to cobalt exchange to give Co/H-MOR. Cobalt oxide within the pores of Na-MOR (25 g) was prepared by 3 × 200 ml cobalt exchange with 0.5 M $Co(NO_3)_2 \cdot 6H_2O$ at 60 °C. Following the final exchange, the excess Co solution was removed by water washing. To a slurry of Co/Na-MOR, NaOH was added slowly keeping the pH about 9. After about 15 min the pH decreased to about 5 and more NaOH was added until the pH remained 9. The catalyst was filtered, washed, dried and calcined as before. The calcined CoO_x/Na-MOR catalyst was black in color. Elemental analysis for Co, Al and Na were obtained by inductive coupled plasma and the number of acid sites were determined by temperature programmed desorption of NH_3 and are given in table 1.

2.2. Catalytic reactions

Catalytic activities and selectivities were determined in a 1.25 cm I.D., quartz, plug-flow micro-reactor at atmospheric pressure. The thermocouple was in contact with the catalyst bed, and the reaction temperature was 300 °C for reduction by propylene and 400 °C for reduction by methane. At each reaction temperature, NO oxidation (or NO_2 decomposition) and NO_2 reduction to N_2 were studied independently. The gas flow rates were controlled by Brooks 5872 mass flow controllers, and the reactant composition was obtained by mixing four different gases (NO/He, NO_2/He, C_3H_6/He or CH_4/He and He). The compositions of the reaction mixtures were 1025 ppm NO and 2.5 wt% O_2 (balance He), 1025 ppm NO_2 and 1000 ppm C_3H_6 (balance He), or 1200 ppm NO_2 and 1000 ppm CH_4 (balance He). Approximately 0.1–0.4 g of catalyst was crushed and screened to 20/40 mesh and the gas hourly space velocity was varied between 2,000 and 27,000 h^{-1} in order to keep the conversion to N_2 between 10 and 30%. The selectivity for N_2 formation ($N_2/(CO_2 + CO)$) was determined at 20% conversion by adjusting the space velocity. In order to minimize background NO oxidation in the lines leading to the micro-reactor, plastic tubing was used. The GHSV was adjusted to give an NO oxidation and NO_2 decomposition conversion of 20–30%. The outlet composition was analyzed by on-line gas chromatography equipped with a TCD detector (5890 HP with an 1/8 in × 8 ft 5A molecular sieve column for O_2, N_2, CO and CH_4 plus a 1/8 in × 6 ft Porapack R column for CO_2 and C_3H_6) and a Rosemont analytical model 591 A chemiluminiscence analyzer.

3. Results

The selective catalytic reduction of NO in excess oxygen was studied with both propylene and methane. Because of its higher reactivity, propylene reacts at significantly lower temperature than does methane. For comparison with previous studies, the reaction temperature was 300 °C with propylene and 400 °C for methane. For each reducing agent, the individual steps in the reaction pathway were measured over catalysts with and without ion-exchanged cobalt. The catalysts included zeolites known

Table 1
Catalyst compositions.

Catalyst	Wt% Al	Wt% Co	Co content (mmol/g)	Wt% Na	H^+ content (mmol/g)
1% Co/H-MOR	2.6	0.75	0.13	–	0.74
1% Co/H-ZSM-5	1.8	0.53	0.09	–	0.56
1% Co/H-USY	10.0	1.28	0.22	0.1	1.54
1% Co/H–SiO_2–Al_2O_3	nd	1.04	0.18	–	0.73
H-MOR	5.8	–	–	–	1.74
1% Co/H-MOR	5.6	0.74	0.13	–	1.50
1% Co/Na-MOR	5.4	0.95	0.16	4.18	0.05
3% Co/H-MOR	5.7	3.15	0.53	–	1.53
4% Co/Na-MOR	5.5	3.80	0.65	2.09	0.68
4% CoO_x/Na-MOR	5.5	4.06	0.69	3.19	0.39

Table 2
NO_x conversion at 300 °C with propylene.

Catalyst	Rate of NO oxidation[a] (10^{-4} mmol/g min)	Rate of N_2 formation[b] (10^{-4} mmol/g min)	Selectivity[c] $N_2/(CO + CO_2)$	Specific rate of N_2 formation (10^{-5} molecules/s H^+)
H-MOR	1.2	26.5	0.27	6.0
1% Co/H-MOR	3.0	24.5	0.28	5.5
H-ZSM-5	6.0	5.5	0.59	1.6
1% Co/H-ZSM-5	7.7	5.0	0.53	1.5
H-USY	0.75	2.5	0.53	0.27
1% Co/H-USY	3.5	3.5	0.43	0.38
H–SiO_2–Al_2O_3	nd	5.4	0.22	1.2
1% Co/H–SiO_2–Al_2O_3	3.3	5.0	0.26	1.1

[a] NO = 1025 ppm, O_2 = 2.5 wt%, balance He, GHSV 4,500–27,000 h^{-1}.
[b] NO_2 = 1025 ppm, C_3H_6 = 1000 ppm, balance He, GHSV 4,500–27,000 h^{-1}.
[c] The conversion to N_2 (from NO_2) was 20%.

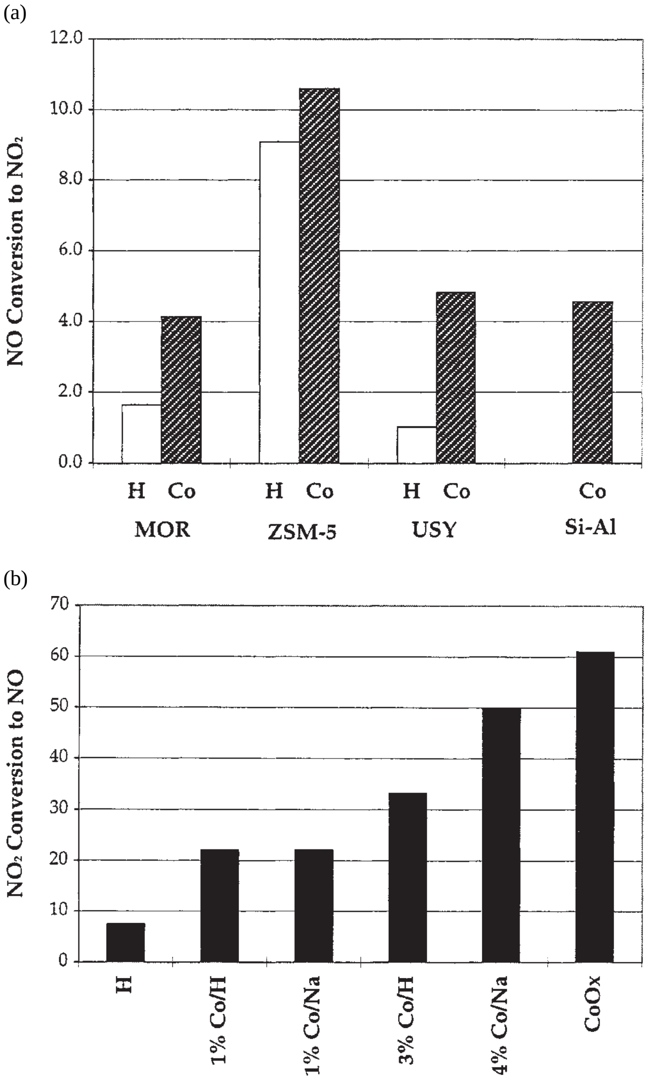

Figure 1. (a) Oxidation of NO to NO_2 at 300 °C, 1025 ppm NO, 2.5% O_2 and 10,000 GHSV. The equilibrium composition is 21% NO–79% NO_2. (b) Decomposition of NO_2 to NO over mordenite catalysts at 400 °C, 1200 ppm NO_2, 2.5% O_2 and 10,000 GHSV. The equilibrium composition is 61% NO–39% NO_2.

for their high activity, like MOR and ZSM-5, and those which are poorly active, like Y-zeolite and silica–alumina. In addition, for MOR both the amount of ion-exchanged cobalt and protons in the catalyst were varied.

The first reaction in the selective catalytic reduction of NO is oxidation to NO_2. At 300 °C, the equilibrium conversion for a mixture of 1025 ppm NO in 2.5% O_2 is 79% NO_2. In the absence of catalyst, the conversion of NO was 4% at the flow rate equivalent to the lowest space velocity in the catalyst tests. This background conversion was subtracted from the catalytic conversion, and the rates of NO oxidation are given in table 2. Comparison of the NO conversion for the catalysts with and without Co are shown in figure 1(a) at a GHSV of 10,000. At 300 °C, the NO conversion is generally less than about 10%, substantially below equilibrium for every catalyst. The activities of the acidic supports are lower than those of the Co catalysts, while the NO oxidation activity of H-ZSM-5 is much higher than the activities of other cobalt-free, acidic supports.

As the reaction temperature increases, the NO_2 concentration at equilibrium decreases. At 400 °C, the equilibrium NO_2 concentration is about 39%, thus determination of the NO oxidation rate becomes increasingly difficult at higher reaction temperatures. Therefore, in order to improve the accuracy, the rate of NO_2 decomposition (in oxygen) was determined, and the NO oxidation rate was calculated from the equilibrium constant. The rates of NO_2 decomposition are given in table 3, and comparisons of the conversions for catalysts with and without Co are shown in figure 1(b). At 400 °C and a GHSV of 10,000 for all ion-exchanged Co^{2+}-MOR catalysts, the decomposition of NO_2 is also below the equilibrium conversion. As observed at 300 °C, the rate of the H-MOR is lower than that of the Co^{2+}-MOR catalysts and increases slightly with increasing Co content. It is notable that the catalyst which contained cobalt oxide exhibits a significantly higher activity than ion-exchanged cobalt-mordenite catalysts and is the only catalyst to establish equilibrium at a GHSV of 10,000. As a result, the rate

Table 3
NO_x conversion at 400 °C with methane.

Catalyst	Rate of NO decomposition[a] (10^{-4} mmol/g min)	Rate of N_2 formation[b] (10^{-4} mmol/g min)	Selectivity[c] $N_2/(CO + CO_2)$	Specific rate of N_2 formation (10^{-5} molecules/s H^+)
H-MOR	0.54	23	0.84	2.2
1% Co/H-MOR	1.6	16	0.75	1.8
1% Co/Na-MOR	1.6	1.7	0.28	5.7
3% Co/H-MOR	2.4	17	0.75	1.9
4% Co/Na-MOR	3.6	6.7	0.64	1.6
4% CoO_x/Na-MOR	12.9	4.1	0.35	1.8
H-USY	nd	1.6	0.89	0.17
1% Co/H-USY	nd	1.8	1.37	0.20
$H–SiO_2–Al_2O_3$	nd	0.5	0.71	0.11
1% $Co/H–SiO_2–Al_2O_3$	nd	0.7	1.09	0.16

[a] $NO_2 = 1200$ ppm, $O_2 = 2.5$ wt%, balance He, GHSV 1,700–19,200 h^{-1}.
[b] $NO_2 = 1200$ ppm, $CH_4 = 1000$ ppm, balance He, GHSV 1,700–19,200 h^{-1}.
[c] The conversion to N_2 (from NO_2) was 20%.

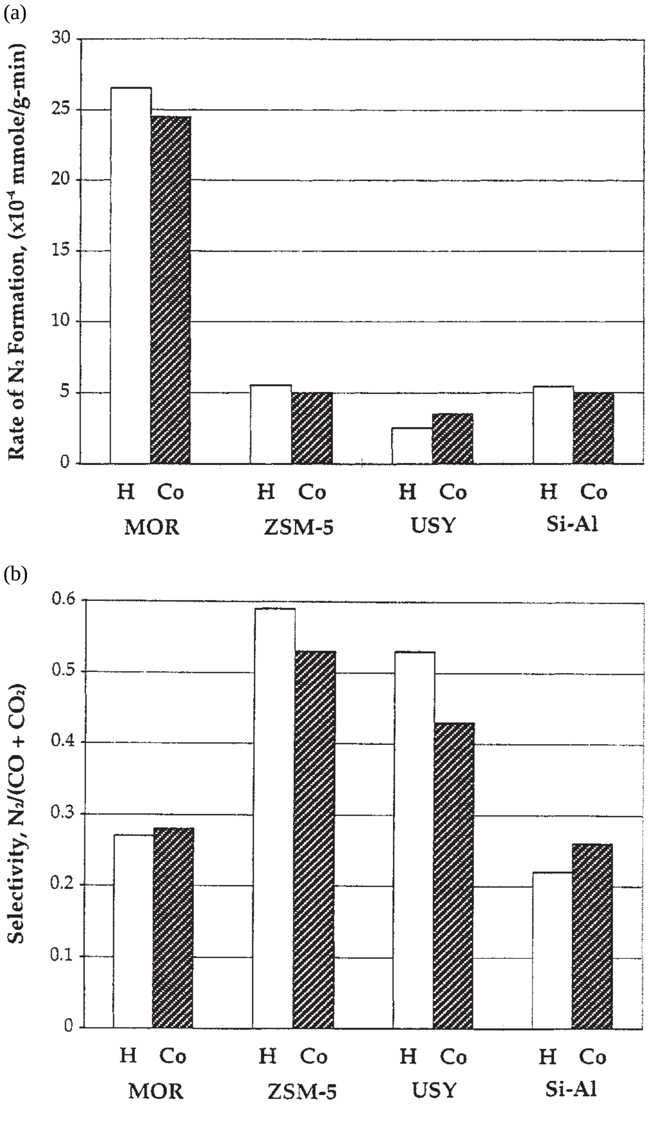

Figure 2. Reduction of NO_2 with propylene at 300 °C, 1025 ppm NO_2, 1000 ppm C_3H_6. (a) Rate of N_2 formation. (b) Selectivity ($N_2/(CO_2 + CO)$) at 20% N_2 conversion.

of NO_2 decomposition for CoO_x-MOR was determined at higher GHSV where the reaction was not in equilibrium.

Subsequent to NO oxidation, NO_2 is reduced to N_2 (and NO) by the hydrocarbon. The rate of N_2 formation by propylene is given in table 2 and shown in figure 2(a) for catalysts with and without Co. In every case, the rate of N_2 formation is nearly identical for catalysts with and without Co. The per g activity of H-MOR is approximately 5 times higher than that of the other catalysts. The selectivities are also given in table 2 and figure 2(b). The selectivities are higher for ZSM-5 and USY and slightly higher for the Co-free catalysts compared to those with Co^{2+}. The implication from both the rate and selectivity is that the formation of N_2 is affected by the acid sites of the support, rather than by the Co^{2+} ions.

Similar comparisons for the rate of N_2 formation by methane for Co-containing and Co-free catalysts are given in table 3 and figure 3. Catalysts with 0.74 and 3.2 wt% Co are slightly less active than H-MOR, while the activities of Co/H-Y and $Co/SiO_2–Al_2O_3$ are much lower than that of Co/H-MOR. Nevertheless, for the latter two catalysts, the activities of the acidic support and Co catalyst are also similar. In addition, as observed for reduction with propylene, the selectivity is slightly higher for H-MOR than Co/MOR. Again, for reduction by methane, both the activity and selectivity are consistent with the suggestion that the acidic supports are the catalytic site for the reduction of NO_2 to N_2.

4. Discussion

4.1. NO oxidation

There is general agreement that the reaction pathway for selective reduction of NO_x proceeds via oxidation of NO to NO_2 followed by the reduction of NO_2 to N_2 [12,13,18–24]. In addition, the rate of NO oxidation over ion-exchanged cobalt-zeolite catalysts is often thought to be rapid and in

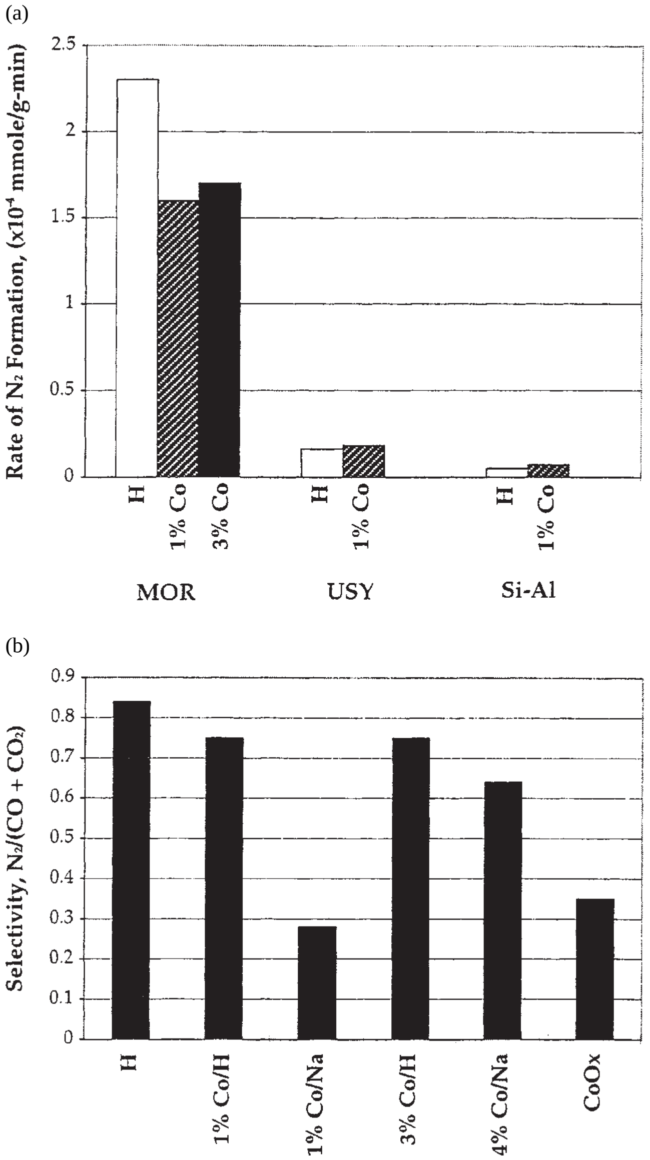

Figure 3. Reduction of NO_2 with methane at 400 °C, 1200 ppm NO_2, 1000 ppm CH_4. (a) Rate of N_2 formation. (b) Selectivity ($N_2/(CO_2+CO)$) at 20% N_2 conversion.

equilibrium with the rate determining step the formation of N_2 [19,20,22,29]. The rate of NO oxidation, however, is dependent on the reaction temperature, space velocity and type of catalyst.

Previous studies of the oxidation of NO over Co/ZSM-5 at a GHSV of 45,000 indicate that equilibrium is not achieved at reaction temperatures below about 450 °C [19]. In that study, however, the calculated equilibrium conversions were too low. Based on the gas composition, we estimate that Co/ZSM-5 does not achieve equilibrium even at 600 °C, and at 400 °C, the approach to equilibrium is only about 40%. (These calculations were verified with the authors of [19] (cf. [30]).)

At space velocities from 4,500–27,000 h^{-1}, the NO oxidation conversion of all ion-exchanged cobalt catalysts is low, generally, less than about 20% and well below the equilibrium value. Comparison of the catalyts at 300 °C and a GHSV of 10,000 (figure 1(a)) demonstrates that the NO conversion is lower on H-zeolites than Co-exchanged zeolites in agreement with the literature [19]. From the rates in table 2, the specific rate per Co can be calculated by subtracting the rate of the support from that of the Co catalyst and normalizing by the amount of Co. Figure 4 shows the specific rates of Co on each support and indicates that Co^{2+} ions on H-ZSM-5, H-MOR, H-USY and $H–SiO_2–Al_2O_3$ have nearly identical activity for NO oxidation. (The activity of $H–SiO_2–Al_2O_3$ was not determined, thus the specific activity of Co^{2+} on $H–SiO_2–Al_2O_3$ is estimated to be high by approximately 25%.) The NO oxidation activity, therefore, is not dependent on the structure or composition of the support, and Co^{2+} ions on zeolite and amorphous supports are equally effective.

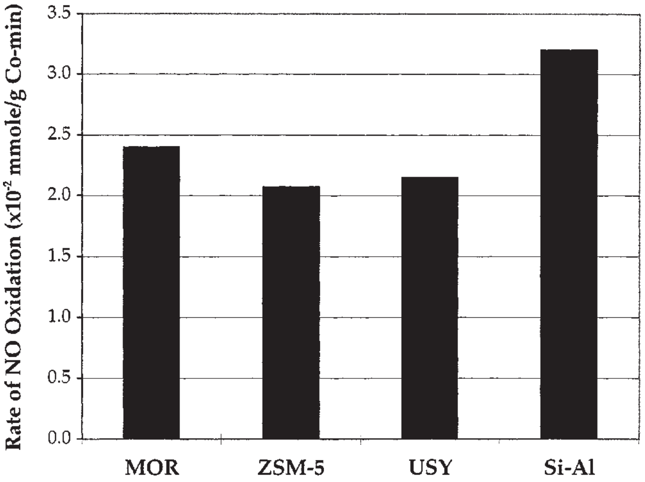

Figure 4. The specific rate (per Co) for NO oxidation at 300 °C, 1025 ppm NO and 2.5% O_2.

At 400 °C and a GHSV of 10,000, the rate of NO_2 decomposition is also not sufficiently rapid to achieve equilibrium for ion-exchanged mordenite catalysts (figure 1(b)). Consistent with the results at 300 °C, the rate of H-MOR is lower than that of Co/H-MOR, and the rate increases with level of Co exchange (table 3). Comparison of catalysts with the same amount of Co but different amounts of protons, indicates that the NO oxidation rate is not strongly dependent on the support acidity, i.e., Co^{2+} ions on H-MOR and Na-MOR are nearly as effective for NO oxidation. Compared with ion-exchanged cobalt, however, cobalt oxide is much more active for NO oxidation in agreement with earlier studies [24].

In general, the order of reactivity for NO oxidation is protons $<$ ion-exchanged Co^{2+} $<$ cobalt oxide [24] and is not strongly dependent on the structure of the support (zeolite or amorphous), or the number and strength of acid sites.

4.2. Reduction of NO_2

With the catalysts and reaction conditions of this study, the rate of NO oxidation is slow. Therefore, in order to determine the effect of acidic support on the rate of N_2 formation, it is necessary to measure the rate of NO_2 reduction, rather than the rate for reduction of NO + O_2. While NO oxidation is catalyzed by Co ions and oxides, figures 2 and 3 indicate that the formation of N_2 is unaffected by these metal species. Rather, the catalysts' activities and selectivities suggest that the reduction by both propylene and methane is catalyzed by support protons. In figures 2(a) and 3(a), H-MOR is more active than the other, Co-free catalysts. If the activity is normalized by the number of acid sites (table 1), the activity per H^+ increases in the order H–SiO_2–Al_2O_3 < H-USY < H-ZSM-5 < H-MOR (table 2) in agreement with previous results [31]. In addition, the differences in the specific rates are much larger for methane than propylene. For example, the activity per H^+ of H-MOR is about a factor of 5 higher than that of H–SiO_2–Al_2O_3 for propylene reduction, but about 20 times higher for reduction by methane. Qualitatively, the specific rate increases with increasing acid strength. For example, the heat of pyridine adsorption is about 140 kJ/mol for H–SiO_2–Al_2O_3, 160 kJ/mol for H-ZSM-5, and 200 kJ/mol for H-MOR [32], while the heat of NH_3 adsorption of Brønsted sites in H-USY is 125 kJ/mol compared to 135 kJ/mol in H-ZSM-5 [33].

In addition to the acid strength, the number of acid sites is also important. In figure 5(a), the rate of N_2 formation (NO_2 reduction by methane) and the N_2/CO_x selectivity are plotted against the number of protons, and in figure 5(b) the rate and selectivity are plotted versus the amount of Co on the various Co/MOR catalysts (data from tables 1 and 3). In figure 5, as the number of protons in H-MOR increase there is a linear increase in both the selectivity and the rate of N_2 formation. A similar correlation between the number of acid sites in ZSM-5 and MOR and the rate of N_2 formation has been given for the selective reduction of NO by propylene [34]. While there is a strong correlation with the number of acid sites, there is no correlation between the rate of N_2 formation, or selectivity, and the amount of Co, either as Co^{2+} ions or CoO_x.

In addition to the formation of N_2, non-selective reduction of NO_2 yields NO. For methane, the two reactions are:

$$2NO_2 + CH_4 \rightarrow N_2 + CO_2 + 2H_2O \tag{1}$$

$$4NO_2 + CH_4 \rightarrow 4NO + CO_2 + 2H_2O \tag{2}$$

For selective reduction, one mole of methane reacts for each mole of N_2 formed, while non-selective reduction leads to oxidation of methane without production of N_2. For H-MOR at 400 °C, the selectivity, $N_2/(CO + CO_2)$, is about 0.8. From the selectivity and the stoichiometries of reactions (1) and (2), one can calculate the fraction of NO_2 which is converted to N_2 and that to NO. For H-MOR, approximately two-thirds of the NO_2 undergo selective reduction. Compared with the H-MOR, Co/H-MOR has a similar, but slightly lower selectivity indicating that Co^{2+} promotes the non-selective reduction of NO_2. This is most apparent for catalysts with a low number of protons, i.e., Co/Na-MOR (table 3). Here the conversion to N_2 is relatively low, due to the low number of acid sites, resulting in a higher contribution from the non-selective reduction by the Co ions.

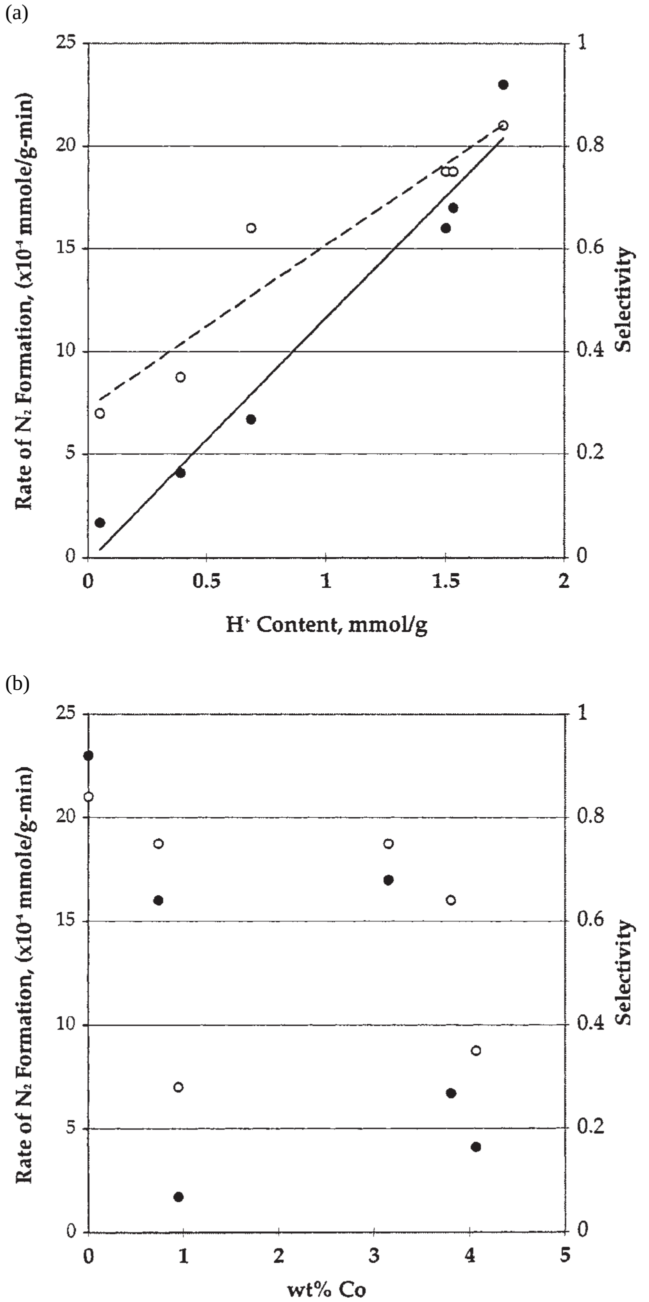

Figure 5. Correlation of the rate of N_2 formation (solid symbols) and N_2/CO_x selectivity (open symbols), 1200 ppm NO_2 and 1000 ppm CH_4 at 400 °C, with: (a) the number of acid sites of mordenite, and (b) wt% Co.

The N_2/CO_x selectivity of the Co/H-MOR catalysts is also higher than those reported for other cobalt-exchanged, zeolite catalysts [19–22]. The previous selectivities, however, were determined for the reduction of NO. As a result, O_2 which is necessary for oxidation of NO can also oxidize the hydrocarbon resulting in CO_2 without formation of N_2, thus lowering the selectivity. While the CH_4 combustion rate is not high over H-MOR and Co/MOR, the N_2/CO_x selectivity will be lower from NO + O_2 than from NO_2.

Although oxidation of CH_4 (by O_2) leads to a lower selectivity, this does not account for the higher selectivity of our catalysts, and a second factor is also important. In the previous catalysts [19–22], the level of cobalt exchange was very high even exceeding the ion-exchange capacity in highly loaded catalysts. As a result, there are likely few protons remaining in the zeolite. Thus, the rate of N_2 formation is relatively low. In addition, the high Co loading increases the rate of non-selective NO_2 reduction. Both effects contribute to the lower N_2/CO_x selectivities compared with our catalysts.

In summary, the above results indicate that NO oxidation is catalyzed predominantly by metal ions and oxides, and cobalt ions on all supports are equally effective. At our reaction temperatures and space velocities, NO oxidation is slow and not in equilibrium. By contrast, the formation of N_2 occurs at the support acid sites, the rate increases linearly with the number of protons, and the specific rate increases as the acid strength increases. Cobalt (2+) ions do not contribute significantly to the formation of N_2, but do non-selectively reduce NO_2 to NO. The selective reduction of NO, therefore, requires two catalytic functions, metal and acid sites.

4.3. Reaction mechanism

Several reaction mechanisms and intermediates have been postulated for the selective reduction of NO_x [3]. One mechanism suggests that NO decomposes to N_2 and O_2 and that chemisorbed O_2 is reduced by the hydrocarbon [35]. An alternative mechanism suggests that the initial step is selective oxidation of the reducing agent [36–38], possibly to a ketone, aldehyde [37], or alcohol [39]. Reaction of this partially oxidized intermediate with NO leads to the formation of N_2. The final mechanism suggests that in the initial step, NO is oxidized by the catalyst to NO_2 [12,13,18,29,20–24]. Because NO_2 is a stronger oxidizing agent than NO (or O_2), it selectively reacts with the hydrocarbon and is reduced to N_2 [17]. Several nitrogen-containing intermediates have been proposed including nitro [13,18,20,23], nitrito [18,23], nitrato [18,23], nitrile [40] and HCN [13].

In each of the above mechanisms, the formation of N_2 is thought to be a redox-process catalyzed by metal ions, or oxides. For example, for the hydrocarbon oxidation mechanism, O_2 is believed to be chemisorbed at the metal site and is selective for partial oxidation. The oxidized intermediates eventually react with NO to form N_2. All steps occur at the metal ion. Similarly, for the NO oxidation mechanism, chemisorbed NO is oxidized to NO_2, and is subsequently reduced by the hydrocarbon. Again all steps are thought to be catalyzed by the metal ions.

The results of this study support the NO oxidation mechanism and indicate that NO oxidation occurs at the metal ion site, in agreement with previous studies. In contrast to the earlier mechanism, however, our results suggest that reduction of NO_2 occurs at the support acid sites, rather than at the metal ion sites. The importance of the acidic support on the activity for selective reduction of NO_x has been previously recognized [4,10,15–17], however, it was thought that either the zeolite acidity, crystal field, or cation location was responsible for changes in the catalytic properties of the metal ion [10,29]. We suggest that the formation of N_2 occurs first by protonation of the reducing agent and that the carbocation, i.e., carbenium and carbonium ions, reacts with gas phase NO_2. A similar reaction sequence was proposed for NO reduction by propylene over metal-free, acidic zeolites [2]. The activation of olefinic reducing agents by the acid sites in metal-exchanged zeolites was also suggested. However, the formation of N_2 was still considered to occur at the metal site [2]. We believe that the formation of N_2 is catalyzed exclusively by protons even for metal-exchanged zeolites. The rate of NO_2 reduction, therefore, is dependent on the ability to form a carbocation and is determined by the number and strength of the acid sites as well as the reducing agent. For example, the rate of N_2 formation increases in the order propylene $>$ propane $>$ methane [19] and is consistent with the ease of protonation of the hydrocarbon. Since propylene is easily protonated, relatively weaker acid sites like those of SiO_2–Al_2O_3 and H-USY are effective for NO_2 reduction. On the other hand, because formation of a carbenium ion from methane is much more difficult, the weaker acid sites of SiO_2–Al_2O_3 and H-USY are not effective, and only catalysts with very strong acid sites, like those in MOR, MFI, FER and BEA, affect the formation of N_2 [1,10,17].

The formation of an adsorbed carbenium ion from methane is also consistent with a primary kinetic isotope effect suggesting that the rate determining step in the formation of N_2 is activation of the C–H bond [20]. This was thought to occur by a H-radical abstraction from CH_4 by chemisorbed NO_2 (at the Co^{2+} ion). However, a primary kinetic isotope effect is also consistent with protonation of methane and formation of a carbenium ion. Once protonated, methane could more readily react with NO_2 leading to organo–nitrogen intermediates and the eventual formation of N_2.

We believe that the selective reduction of lean NO_x requires two independent catalytic sites, metal ions and oxides for NO oxidation and strong acids for reduction of NO_2, and if either function is missing, the catalyst will have poor activity. Furthermore, since either reaction may be rate limiting, development of improved catalysts may require increasing the activity of either the metal, or acid site. Which reaction is rate limiting, or how changes in the catalyst composition affect the catalyst performance, can be determined by studying the rate of the individual reactions in the selective reduction pathway.

5. Conclusion

The selective reduction of NO_x by both propylene and methane indicates that NO is oxidized to NO_2 prior to reduction to N_2. NO oxidation is catalyzed predominantly by metal ions and oxides, and cobalt oxide is much more active than cobalt ions. At 10,000 GHSV and reaction temperatures below about 400 °C, the NO oxidation rate of ion-exchanged cobalt catalysts is slow and not in equilibrium. In addition, the NO oxidation activity of ion-exchanged cobalt is little affected by the number and strength of the acid sites. While NO oxidation occurs primarily at metal sites, the formation of N_2 occurs at the acid sites. Both the rate of N_2 formation and selectivity increase linearly with the number of protons, and the specific rate increases as the acid strength increases. It is suggested that the formation of N_2 occurs by protonation of the reducing agent followed by attack of the carbocations by gas phase NO_2. The selective reduction of NO, therefore, requires two, independent catalytic functions, metal and acid sites.

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